NUCLEAR MAGNETIC RESONANCE AND INFRARED STUDY OF TRIPHENYLENE

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ABSTRACT. Proton magnetic resonance studies of solid triphenylene were made between 140°K to its melting point. The experimental second moment is found in well agreement with that estimated for rigid lattice configuration. The possibility of some additional quenching process at higher temperature as vibrational motion and lattice expansion has also been reported.

In infrared spectrum of triphenylene there is a strong band in the C–H out of plane bending region at 740 cm^{-1} and two medium bands at 1500 cm^{-1} and 1440 cm^{-1} due to C=C stretching.

INTRODUCTION

Measurements of the variation with temperature of NMR absorption line shape in solid can give valuable informations regarding the various molecular motions and diffusion processes which may be occurring in the solid state. The molecular motion causes a reduction of local magnetic field and thus of the resonance line width (Gutowsky and Pake, 1950). The evidence of such rotation is also obtainable from X-ray or dielectric measurements. The X-ray measurements only give such information if each molecule spends most of its time rotating whereas the nuclear resonance linewidth will be affected even though each molecule spends a very small fraction of its time rotating. Dielectric measurements are only applicable to polar molecules, whereas nonpolar molecules are most likely to rotate on account of their greater symmetry.

The NMR studies of hydrocarbons are of particularly interest because the high gyromagnetic ratio of the proton ensures a relatively large signal strength and the zero spin of ^{12}C simplifies the interpretation of the results. Triphenylene was chosen to study because of its known X-ray structure and of its triplet li fe time measurements which suggest about some additional quenching processes occurring at higher temperatures, these processes may include molecular rotation and diffusion of molecules.

Pinnock, Taylor and Lipson (1956) have shown that the structure of triphenylene, firstly determined by Klug (1950), had the molecules correctly oriented but incorrectly positioned in the unit cell. Later a detailed analysis of the structure of triphenylene by X-ray method was published by Ahmed and Trotter

(1963). The crystals of triphenylene are orthorhombic with four molecules in a unit cell of dimensions $a = 13{\cdot}17$, $b = 16{\cdot}73$, $c = 5{\cdot}26$ and space group $p2_12_12_1$. The point group molecular symmetry was 62 m. Figure 1 shows the bonds length

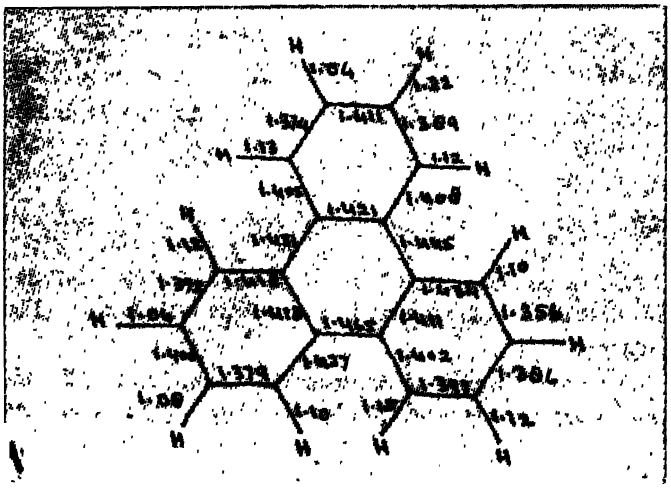

Figure 1. Bond distances of triphenylene molecule.

and angles within the experimental errors. The mean value for C–H length is 1·11Å. The present paper reports the wide line NMR and infrared investigations of triphenylene. The experimental data have been analysed in terms of existing theories.

EXPERIMENTAL DETAILS

The NMR experiment was performed using a Varian Associates variable frequency spectrometer and 12 inches magnet system. The resonance was observed at 15 Mc/sec. The temperatures over a range of 140°K to the melting point of the sample were obtained by use of a Varian model V-4340 variable temperature NMR probe accessory, utilizing a flow of heated or cooled nitrogen gas over the sample and it was necessary to encapsulate the powder in glass capillary tube. The NMR records were taken at Tata Institute of Fundamental Research, Bombay.

The infrared spectrum of triphenylene was recorded on the Perkin-Elmer Infracord model 137 spectrophotometer with sodium chloride optics in the range 4000 to 630 cm^{-1}. The instrument was caliberated by recording the standard atmospheric water vapour band at 3740 cm^{-1}. The spectrum of triphenylene was recorded in KBr at room temperature. The record was taken at central Drug Research Institute, Lucknow.

The sample of triphenylene used in our investigations was supplied by Chemische Fabrik, Fluka (Switzerland) and was of purum quality.

CALCULATIONS AND RESULTS

(i) *Rigidlattice*

The experimental second moments were calculated from these derivative traces using the trapezium rule and applying a correction for the fine modulating

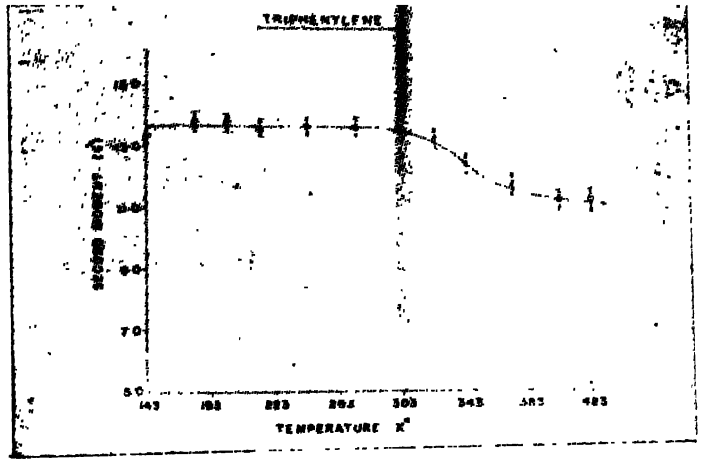

Figure 2. The variation of secondmoment against temperature.

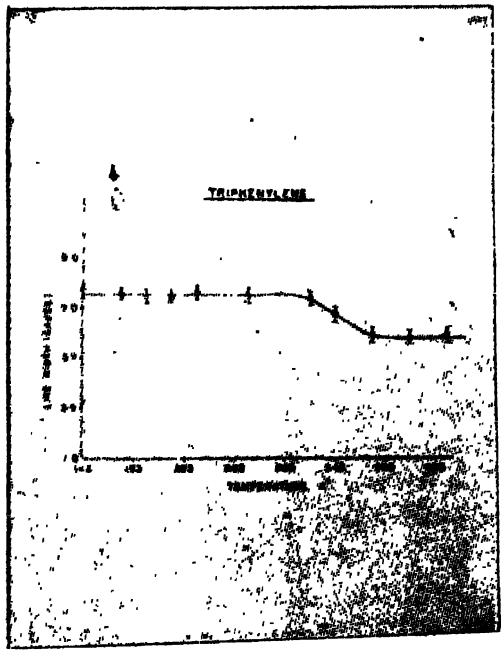

Figure 3. The variation of resonance linewidth with temperature.

field (Andrew 1953). The line width is defined as the separation between the pairs of peak in the observed derivative of absorption line. The second moment values and line widths have been plotted as a function of temperature in figures (2) and (3) respectively.

The theoretical rigid lattice value for the second-moment for protons of a polycrystalline sample consists of two parts—the intramolecular contributions which arise due to the nuclei residing in the same molecule and intermolecular contributions which are due to the interactions between protons residing in different molecules. The intramolecular contribution to the second moment for protons was given by Van Vleck (1948) as :

$$S_1 = \frac{6}{5} \frac{(I+1)^2}{I} N^{-1}\mu^2 \sum_{>k} r_{jk}^{-6} \text{ gauss}^2$$

where I is the spin number, N is the number of magnetic nuclei over which the sum is taken, μ is the magnetic moment of proton, and r_{jk} is the internuclear distance between the nuclei j and k. Using Bearden and Watt's (1951) values of physical constants, the above equation simplifies as :

$$S_1 = \frac{715{\cdot}9}{N} \sum_{j>j} r_{jk}^{-6} \text{ gauss}^2$$

Thus the intramolecular contributions to the second moment can be calculated reasonably accurately for any given molecular structure and found to be about 1.756 gauss^2 for the crystal of triphenylene. It seems to be some what high but it is due to the intra molecular over crowding occurring due to close approaches of hydrogen atoms attached to 2, and 5, 8 and 11, 14 and 17 carbon atoms. The distances between carbon atoms 2 and 5, 8 and 11, 14 and 17 are 2·93, 2·91 and 2·92 Å respectively which show the intramolecular overcrowding about equally in all three regions.

An accurate evaluation of the intermolecular contributions to the second moment necessitates a knowledge of the disposition of the molecule in the lattice. It can be estimated from the values calculated for other hydrocarbons when the complete crystal structure is not known. Andrew and Eades (1953) estimated the intermolecular contribution to the second moment about 10 gauss^2 for cyclohexane. If it is assumed that the ratio of intermolecular contributions of the two compounds is the same as the ratio of number of protons in them, a value of about 10 gauss^2 can also be estimated for triphenylene.

The theoretical rigid lattice value of second moment for triphenylene is thus estimated about 11.756 gauss^2. The experimental value at 143°K is observed to be about 13·7 gauss^2—a value which is in good agreement with the calculated rigid lattice value and no important change in resonance lines is observed from

143°K to 323°K. However this invariancy of second moment and line width breaks down at higher temperatures.

(ii) *Molecular Reorientation*

An examination of the lattice structure suggests that the narrowing of the absorption line, in turn the reduction in the value of second moment, can be explained on the basis of molecular reorientation. The effect of the motion on second moment was calculated using the method first suggested by Gutowsky and Pake (19. A rough value of the second moment for the reorientation of the molecular about the centre of gravity can be obtained by replacement of r_{jk} by the centre to centre molecular separation in Van Vleck's expression for intramolecular contribution to the second moment i.e., by concentrating all nuclear magnets at their molecular centres. The perpendicular distance between the molecules of triphenylene (Ahmed and Trotter, 1963) is found about 3·37 Å.

Andrew and Eades (1953) have also suggested that the rotation of the molecule about corresponding axis reduces the intermolecular contribution by a factor 0·24. This gives a value of 2·4 Gauss^2 for rotational intermolecular contribution to the second moment.

IETERPRETATION OF RESULTS

The second moment and linewidth are plotted as a function of temparature in figures 2 and 3 respectively. The constant portion of the secondmoment *vs* temperature curve corresponds to the calculated second moment of the rigid lattice state where all the molecular motion is supposed to have been frozen. This constant region (from temperature 143°K to 303°K) has the mean second moment value to be obout 13.7 ± 1.0 gauss^2 which is in good agreement with the theoretically calculated value (11.756 gauss^2). The result leads to the conclusion that lattice is effectively rigid below 303°K. Thus our second moment data are consistent with X-ray studies and support our assumed model of the crystal and molecular structure.

The slight reduction in second moment and linewidth at above 303°K can be explained as due to lattice expansion and to some vibrational motion as observed in the case of naphthalene molecule (Andrew 1950). The interpretations of Gutowsky and Pake (1950) and Andrew and Eades (1953) regarding the fall in the value of second moment due to the molecular rotation do not satisfy the present reduced secondmoment, even very near to melting point of the sample. However, Ahmed and Trotter (1963) with their X ray measurements, suggestgd a regular distortion of the molecule from a planar configuration, with the atoms of ring *B* and *C* being displaced in the same direction and those of ring *A* in the opposite direction. According to them this distortion might be due to intra or intermolecular steric effect (or both). Such distortion, however, were not observed in biphenyl (Trotter 1961) where similar steric interferences

were present (except that in phenyl the central bond is rather longer than bond such as 9–10 in triphenylene) and where the molecule might be expected to distort more easily. Therefore, a slight twisting of each of the outside rings in triphenylene might be the expected distortion since this would give a more symmetrical relief of the steric strain. Moreover, the intermolecular C–C and C–H distances corresponds to normal vander waals interactions and there are 15, C-C approaches which are less than 3.7 Å. The non-planarity of the molecule of triphenylene could scarcely be due to these approaches alone, for any strain introduced by these contracts could more readily be relieved by a slight reorientation or vibration of the whole molecule.

According to Andrew and Jenks (1962), if by varying the temperature the parameters of the system is changed on account of increased vibrational amptitude and lattice expansion, the second moment will never be rigorously constant. The invariancy of the secondmoment breaks down at higher temperatures at which the correction frequency of the motion becomes comparable with the resonance frequency. This is why the line width and secondmoment undergo a small narrowing between 303°K and 423°K.

Kellogg and Schwenker (1966) while measuring the triplet life time of triphenylene as the function of temperature. observed that value of triplet life time for triphenylene, decreases with temperature slowly at lower temperature and more rapidly at higher temperature. It falls to about half of its lower temperature value at 298°K. Since life time are entirely governed by either radiative decay or nonradiative decay. It followed that this temperature effecr was not of nonradiative characteristic. Therefore, Siebrand (1967) attributed this observed temperature effect due to some additional quenching processes which may include vibrational motion of the molecule. This gives on added support to our views of vibrational motion and lattice expansion in the case of triphenylene molecule.

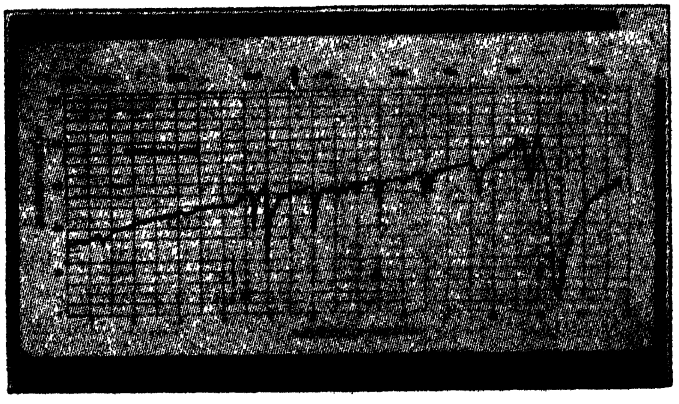

Figure 4. The infrared absorption spectrum of triphenylene at 26°C.

INFRARED STUDY

The infrared absorption spectrum of triphenylene figure (4) shows weak C–H stretching band at 3075 cm^{-1}, while the medium bands at 1500 cm^{-1} and 1440 cm^{-1} seems to be due to C = C stretching. There are two weak bands at 1250 cm^{-1} and 1055 cm^{-1} showing C–H in plane deformation and a strong band in the C–H out-of-plane bending region at 740 cm^{-1} (1,2,-disubstituted benzene).

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REFERENCES

Ahmed, F. R. and Trotter, J., 1963, *Acta cryst.*, **16**, 503.
Andrew, E. R., 1953, *Phys. Rev.*, **91**, 425.
Bearden, J. A., and Watts, H. M., 1951, *Phys. Rev.*, **81**, 73.
Andrew, E. R., and Eades, R. G., 1953, *Proc. Roy. Soc.*, **216A**, 398.
Andrew, E. R., and Jenks, J. G., 1962, *Proc. Phys. Soc.* (*Lond.*), **80**, 663.
Anderson, P. W., 1954, *J. Phys. Soc.* (*Japan*), **9**, 316.
Gutowsky, H. S. and Pake, G. E., 1950, *J. Chem. Phys.*, **18**, 162.
Kellogg, R. E. and Schwenker, 1964, *J. Chem. Phys.*, **41**, 2860.
Klug, A., 1950, *Acta. cryst.*, **3**, 165.
Pinnock, P. R., Taylor, C. A. and Lipson, H., 1956, *Acta. cryst.*, **9**, 173.
Siebrand, W., 1967, *J. Chem. Phys.*, **117**, 2411.
VanVleck, J. H., 1948, *Phys. Rev.*, **71**, 1168.